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HAZARDS FROM COMMON GASES AND VAPORS ENCOUNTERED AT SURFACE DISASTERS

BY

G. W. JONES

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HAZARDS FROM COMMON GASES AND VAPORS ENCOUNTERED AT SURFACE DISASTERS[1]

By G. W. Jones[2]

INTRODUCTION

One of the major activities of the Bureau of Mines is the promotion of safety in mining and other industries. In this connection, the Bureau determines the explosion hazards of combustible gases, vapors, and solids and investigates means of controlling and preventing explosions.

Many dangers are likely to confront men who must enter a building immediately after it has been damaged. Rescue workers must watch constantly for common gases and vapors that may be present in dangerous concentrations in and about demolished buildings. Fuel gas is the most common source of danger, although refrigerants, gases from furnaces, flues, fires, sewers, and industrial processes, and gas from bomb explosions in confined places also constitute definite hazards. To rescuers and trapped casualties, these gases offer the hazards of (1) explosion, (2) toxic effects, including asphyxiation and death, and (3) displacement of air so that the oxygen content of the atmosphere is reduced to or below the danger level.

Although the likelihood of bombing raids on the United States seems remote at present, reports from countries that have undergone them indicate a similarity between such disasters and many of those that occur from causes not associated with war-time. Regardless of the causes, however, persons are trapped beneath structural debris, and rescue workers are necessary to release them. If such services are not provided, should prove inadequate, or are not performed skillfully, victims will die needlessly.

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The purpose of this paper is to provide information on the flammability of the common gases and vapors so that rescue workers may be informed and take the necessary precautions to protect themselves and, if possible, the live victims who must be rescued.

DEFINITIONS

An explosion may be regarded as a chemical reaction which exerts a sudden pressure on its surroundings when suitably activated. This definition applies to both solid and gaseous explosive reactions. In the case of solids, as, for example, a high explosive, the time for complete reaction is exceedingly short; therefore, the pressure developed on the surroundings is very great. The activating agent usually is a detonator of some type.

In the case of gaseous mixtures, the time required to complete the reaction may be very short or long, depending on the type and concentration of the combustibles present in the mixture and the environment in which the reaction takes place. The activating agent for gaseous mixtures usually is a flame, a spark, or a heated material of some type.

To explain what is meant by flammable limits, let us take, for example, an explosive mixture of methane and air. This mixture may be diluted with air, or methane may be added until the mixture will not propagate flame when ignited. These limiting or borderline mixtures that will just propagate flame are designated as flammable limits. There are, therefore, two flammable limits - a lower one of 5 percent and an upper of 15 percent for methane in air. Mixtures within these limits liberate enough energy upon combustion of any one layer to ignite the neighboring layer of unburned gas and are therefore capable of self-propagation of flame; others are not.

Some authorities regard explosive limits as those limiting mixtures within which flame is propagated throughout the mixture, pressure is developed, and more or less violence produced; whereas, limits of inflammability or flammable limits refer only to the passage of flame through the mixture without regard to the development of pressure.

It is impossible to distinguish a burning from an explosion by the amount of violence produced. Mixtures just within the limits of flammability, if confined in a long tube and tested for flammability by opening one end and igniting the mixture at this open end, will propagate flame quietly and slowly through the tube (usually at a uniform speed); and the speed for a given concentration of combustibles in air will vary with the direction of flame propagation. This same mixture, if confined to a

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closed bomb and ignited when the gases are in motion or gentle turbulence, will propagate flame at a speed many times as fast as that in the open-tube experiment and will develop pressures of 30 pounds or more per square inch above atmospheric. Thus, the violence and pressure developed by a flammable mixture depend on the environment and direction of flame propagation; therefore, no differentiation should or can be made between explosive and flammable limits.

FACTORS AFFECTING LIMITS OF FLAMMABILITY

Only a brief discussion of the various factors that affect the limits of flammability of combustible gases and vapors will be given. The limits are affected by the direction of flame propagation: For example, wider limits are obtained for upward propagation of flame than for horizontal or downward propagation; therefore, the risk of an explosion is greater when an atmosphere is ignited near the floor level than when ignited at or near the top.

The limits are widened as the diameter of the apparatus is increased, rapidly at first and then more slowly as the diameter approaches 2 inches. Apparatus larger than 2 inches in diameter gives limits very little different from those obtained with 2-inch apparatus.

The apparatus must be long enough to insure continued propagation of flame after the heat imparted to the mixture by the source of ignition has been dissipated. Apparatus 3 feet or more in length is suitable.

If the apparatus is closed when the mixtures are ignited, and ignition is initiated near the closed end, the lower limit of a mixture is reduced to some extent.

Ordinary variations of laboratory temperatures have no appreciable effect upon the limits of combustible gases.

Normal variations of laboratory pressure have no appreciable effect upon the limits. The effect of high pressures upon the limits is neither simple nor uniform but is specific for each flammable mixture. As yet, no means has been developed for predicting the effect of high pressures upon the limits for any given combustible in air.

The normal quantity of water vapor present in atmospheres at laboratory temperatures affects the lower limit only slightly. Its presence reduces the upper limit, because some of the oxygen in the mixture is displaced by the water vapor; and, since the oxygen concentration is the important factor in an upper-limit mixture, as the oxygen is lowered, the

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amount of combustible that can be burned is decreased, and so the limit is lowered.

Limits of flammability concern the capability of the mixture to propagate flame, not ability of the source of ignition to initiate flame; therefore, if a weak source of ignition is employed, some flammable mixtures, especially those near the limits, may not burn. On the other hand, such strong sources of ignition may be employed that the caps of flame produced (especially in apparatus of small capacity) may give the appearance of flame propagation, yet may not continue to propagate flame after the heating effects of the ignition source are dissipated. Under such conditions, limits of ignitibility and not the true limits of flammability are being determined.

Four basic factors contribute to the causing of explosions, and these must be well-understood by rescue personnel whose duties require that they operate and work in places where combustible gases and vapors may be present:

a. Combustible materials
   - Gases
   - Liquids
     - Vapors
     - Mists
   - Solids

b. Oxygen supply
   - Normal air
   - Oxygen

c. Ignition sources
   - Flame
   - Sparks
   - Heated materials

d. Distribution of oxygen with respect to the combustibles.

The first requirement is that combustible materials be present. These may be divided into gases, liquids, and solids.

Combustible Gases

Combustible gases may be broken down into fuel gases, comprising natural gas, coke-oven gas, coal gas, oil gas, carburetted water gas, water gas, producer gas, and blast-furnace gas. Typical gases of these

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types are listed in table 1. It may be seen that all have specific gravities lower than that of air, so that, when released into a space, they will tend to rise and diffuse rather quickly into the atmosphere above the point of leakage. All produce highly explosive mixtures when mixed with air within the explosive range given in the table. The oxygen content of the different fuel gases is below 1.0 percent; therefore, they may be classed as suffocating gases. With the exception of the natural gases, they are also highly toxic.

Refrigerating gases may be encountered by rescue workers, and the more common ones are listed in table 2, the nonexplosive refrigerants at the top. They comprise the gases carbon dioxide, Freon 11, Freon 12, and sulfur dioxide. The remaining refrigerants are combustible materials that produce explosive mixtures when mixed with air in the proportions given.

It will be observed that, with the exception of ammonia, all the refrigerants in the gaseous state have specific gravities higher than air and in some instances three to four times as heavy. The densities of the gases are important owing to the fact that if they are released in closed spaces (as, for example, in open walls and stairways), the heavy gases flow downward into lower areas, such as cellars, tunnels, and similar places. Rescue workers may go into areas contaminated with these heavy vapors without being aware of their presence, as only sulfur dioxide and ammonia have a sufficiently strong odor in dilute concentrations to indicate their presence.

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TABLE 1. - Composition and explosive limits of typical fuel gases

Type	Composition, percent by volume								Specific gravity, air = 1	Explosive Limits	
	CO_2	C_2H_4	O_2	H_2	CO	CH_4	C_2H_6	N_2		Lower	Upper
Natural gas 1	0.7	0.0	0.0	0.0	0.0	87.3	9.0	3.0	0.62	4.90	15.00
Natural gas 2	.0	.0	.0	.0	.0	83.4	15.8	.8	.64	4.60	14.60
Natural gas 3	.1	.0	.0	.0	.0	68.5	29.5	1.9	.71	4.30	14.25
Coke-oven gas	1.9	3.5	.4	51.1	6.1	31.5	--	5.5	.40	4.75	30.00
Coal gas	2.4	3.0	.8	48.0	7.3	27.2	--	11.3	.47	5.25	33.00
Oil gas.....	2.8	3.8	.3	53.6	10.0	26.2	--	3.3	.41	4.75	32.50
Carburetted water gas	3.2	9.4	.6	36.0	33.3	12.7	--	4.8	.64	5.50	36.00
Water gas	5.4	.0	.7	47.3	37.0	1.3	--	8.3	.57	7.00	72.00
Producer gas	6.1	.0	.4	14.3	25.1	1.9	--	52.2	.87	17.50	70.00
Blast-furnace gas ...	10.7	.0	.5	2.0	27.5	.3		59.0	1.01	39.00	73.50

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TABLE 2. - Explosive limits of refrigerants

Refrigerant	Formula	Specific gravity, air = 1	Soluble in water	Odor	Explosive limits percent by volume	
					Lower	Upper
Carbon dioxide.	CO_2	1.52	Partly	No	Nonexplosive	
Freon 11	$CFCl_3$	4.74	No	Faint	Do.	
Freon 12	CF_2Cl_2	4.18	No	do.	Do.	
Sulphur dioxide	SO_2	2.21	Yes	Strong	Do.	
Ammonia	NH_3	.59	Yes	do.	16.0	25.0
Butane.....	C_4H_{10}	2.01	No	Faint	1.9	8.4
Isobutane	C_4H_{10}	2.01	No	do.	1.8	8.4
Ethyl bromide..	C_2H_5Br	3.76	No	Moderate	6.7	11.2
Ethyl chloride..	C_2H_5Cl	2.23	No	Faint	4.0	14.8
Methyl bromide	CH_3Br	3.27	No	Moderate	13.5	14.5
Methyl chloride	CH_3Cl	1.74	No	Faint	8.2	18.7
Propane	C_3H_8	1.51	No	do.	2.4	9.5

A third subdivision of combustible gases and vapors is given in table 3. This list comprises a wide variety of combustibles that may at times be encountered in rescue work, such as gasoline, benzol, aldehydes, alcohols, ethers, esters, and miscellaneous gases (hydrogen, carbon disulfide, and hydrogen sulfide) not covered in the previous tables. Some of these can be identified by their characteristic odors, whereas others are almost odorless.

The alcohols, ketones, and aldehydes are soluble in water, and their vapors may be removed from underground spaces by directing streams of water into the space. For the others listed, water is ineffective.

The specific gravities of the gases and vapors listed have a wide range. Hydrogen, for example, is only about one-fourteenth as heavy as air, whereas gasoline vapor is 3.5 to 4.0 times as heavy.

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TABLE 3. - Explosive limits of combustible gases and vapors

Combustible	Formula	Specific gravity, vapor, air = 1	Specific gravity, liquid, water = 1	Soluble in water	Explosive limits, percent by volume		Odor
					Lower	Upper	
Acetaldehyde	C_2H_4O	1.52	0.78	Yes	4.00	57.00	Strong.
Acetone	C_3H_6O	2.00	.79	Yes	2.55	12.80	Moderate.
Acetylene	C_2H_2	.91	Gas	Partly	2.50	80.00	Characteristic.
Amylacetate	$C_7H_{14}O_2$	4.49	.88	Yes	1.12	-	Do.
Benzol	C_6H_6	2.77	.88	No	1.35	6.75	Do.
Carbon disulfide	CS_2	2.64	1.26	No	1.25	50.00	Do.
Carbon monoxide	CO	.97	Gas	No	12.50	74.20	No.
Ethyl acetate	$C_4H_8O_2$	3.04	.90	Partly	2.18	11.40	Fruity.
Ethyl alcohol	C_2H_6O	1.59	.79	Yes	3.28	18.95	Characteristic.
Ethylene	C_2H_4	.97	Gas	Slightly	2.75	28.60	Moderate.
Ethyl ether	$C_4H_{10}O$	2.56	.71	do.	1.85	36.50	Anesthetic.
Gasoline	-	3.5-4.0	.71-.75	No	1.40	7.50	Characteristic.
Hydrogen	H_2	.07	Gas	No	4.00	74.20	No.
Hydrogen sulfide	H_2S	1.19	Gas	Partly	4.30	45.50	Characteristic.
Methane	CH_4	.55	Gas	No	5.00	15.00	No.
Methyl acetate	$C_3H_6O_2$	2.56	.92	Partly	3.15	15.60	Fruity.
Methyl alcohol	CH_4O	1.11	.79	Yes	6.72	36.50	Characteristic.
Pentane	C_5H_{12}	2.48	.63	No	1.40	7.80	Moderate
Toluol	C_7H_8	3.14	.87	No	1.27	6.75	Do.
Xylol	C_8H_{10}	3.66	.88	No	1.00	6.00	Do.

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A fourth subdivision comprises the so-called "soil gases," sewage gases, gases from fermentation processes, gases produced by heated insulation, gases from burning wood and paper, and gases from explosives. Typical example of these are given in table 4.

Soil gases may be encountered in sewers and tunnel operations and, as the table indicates, contain high percentages of carbon dioxide and nitrogen and low percentages of oxygen. In most instances, these gases do not form explosive mixtures when mixed with air. Because of their low oxygen content, they are designated as suffocating gases. They are formed by bacterial action between air and certain organic matter in the soil. When oxygen is present, some bacteria convert the carbon of the organic matter to carbon dioxide with the formation of only small concentrations of methane, as indicated samples 1 and 2.

If the bacterial action takes place in the absence of oxygen, one of the products is methane. An example of this type is indicated by sample 3 in which 10.5 percent of methane is present and has calculated explosive limits ranging from 49 to 55 percent.

Samples 4 and 5 are examples of mixtures of soil and natural gas and are highly explosive when mixed with the proper proportions of air.

Samples 6, 7, and 8 are typical of gases produced by the bacterial decomposition of sewage, starch, and cellulose materials. At times such gases may be encountered by rescue workers. They are chiefly carbon dioxide, hydrogen, and methane. The carbon dioxide content may range from 25 to about 80 percent, methane from virtually nothing to 68 percent, and hydrogen from zero to 32.5 percent. All form highly explosive mixtures with air.

Heated insulating material (sample 9) liberates a complex mixture of gases, which are highly explosive, suffocating, and toxic.

Samples 10 and 11 are examples of gases liberated by burning wood and paper. They are incapable of producing explosive mixtures with air but, because of their low oxygen content, are classed as suffocating gases and, owing to the high percentages of carbon monoxide present, are toxic.

Samples 14 and 15 are examples of the composition of the gases liberated by the detonation of high explosives. Bombs may explode deep underground, and high concentrations of the gaseous products of detonation may remain in the debris in which rescue squads may be compelled to operate. As indicated, the gases are highly explosive when mixed with air, and this fact must be kept in mind when entering recently bombed areas.

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TABLE 4. - Composition and explosive limits of miscellaneous gases

Sample	Type	Composition, percent by volume								Explosive limits, percent by volume		Remarks
		CO_2	C_2H_4	O_2	H_2	CO	CH_4	C_2H_6	N_2	Lower	Upper	
1	Soil gas	16.6	0.3	1.0	0.2	0.0	3.2	0.0	78.7	Nonexplosive		Suffocating.
2	do	9.6	.0	5.9	.0	.0	.2	.0	84.3	do.		Do.
3	do	6.8	.7	6.0	.0	.0	10.5	.0	76.0	49.0	55.0	Do.
4	Soil + natural gas	8.0	.2	5.9	.0	.0	18.4	5.0	62.5	20.0	39.0	Do.
5	do	.6	.0	6.7	.0	.0	52.5	12.1	28.1	7.0	22.0	Do.
6	Sewage gas	25.2	.0	.1	.0	.0	67.8	.0	6.9	7.5	19.0	Do.
7	Fermentation gas, cellulose	79.1	.0	.0	6.2	.0	14.7	.0	.0	26.5	38.5	Do.
8	Fermentation gas, grain	65.4	.0	.0	32.5	.0	.1	.0	2.0	13.0	66.0	Do.
9	Gases from heated insulation	1.9	17.4	.0	28.5	2.2	45.3	.3	4.4	4.5	21.5	Suffocating and toxic.
10	Gases from burning wood	6.4	.6	9.4	.0	3.5	.3	.0	79.8	Nonexplosive		Do.
11	Gases from burning paper	7.6	1.2	7.7	.0	6.2	.0	.0	77.3	do.		Do.
12	Soil + coal gas	3.0	1.2	12.2	7.1	4.4	11.8	2.2	58.1	18.0	66.5	Toxic.
13	Automobile exhaust gas	10.7	.0	.9	1.6	4.6	.8	.0	81.4	Nonexplosive		Suffocating and toxic.
14	Gases from explosives, TNT	6.4	.0	.0	26.9	53.2	.2	.0	13.3	9.5	72.0	Do.
15	do	1.5	.0	.0	19.9	60.7	2.3	.0	15.6	10.0	67.0	Do.

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Combustible Liquids

The ability of a combustible liquid to form explosive mixtures is determined by its vapor pressure and is roughly determined by its flash point. The flash point usually is defined as the minimum temperature at which a liquid gives off enough vapor to form a flammable mixture in contact with air. The higher the flash point, the more safely the combustible may be handled and used. All combustible liquids having flash points lower than the temperature at which they are used will, under certain conditions, create explosive mixtures in contact with air. All of the combustible liquids listed in table 2 have low flash points and therefore may produce explosive mixtures at ordinary temperatures. Kerosene is an example of a combustible liquid having a flash point above 100° F. This combustible is relatively free of explosion hazards at temperatures below 100° F.

Combustible Mists

A liquid such as fuel oil, having a high flash point cannot form explosive mixtures at ordinary temperatures in contact with air. If, however, the fuel oil is sprayed or broken up into a fine mist or fog, such mixtures may be explosive in air. The explosion hazard is temporary, because the mist soon coalesces into larger droplets and settles out of the atmosphere. Rescue workers will not encounter explosive mists except very rarely where combustible liquids under pressure may be sprayed into the surrounding atmosphere.

Combustible Solids

The title of this paper excludes the explosibility of combustible solids. It may be said that there is an unlimited number of combustible dusts that, when dispersed into air in the right proportions, form highly explosive mixtures. Rescue workers may encounter such hazards when working in plants where coal, cork, starch, and similar dusts may be present. Also around plants where aluminum, magnesium, zirconium and similar dusts may be present.

Oxygen Supply

As an explosion is an oxidation process, a second important requisite for the production of explosions is an adequate supply of oxygen. From the standpoint of the rescue worker, we are interested only in the supply of normal air. It may be assumed that under virtually all conditions there will be an unlimited supply of air to carry through the oxidation processes. Normal air contains 20.93 percent of oxygen by volume, 0.03 percent of

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carbon dioxide, and the remainder nitrogen and the rare gases. It is interesting to note that the percentage of oxygen in normal air is the same in all parts of the world. Samples of the atmosphere have been taken on land, at sea, and at high and low altitudes, yet precise analyses have shown that the oxygen content does not vary more than a few hundredths of a percent, provided the atmosphere is not contaminated by industrial and other contaminating gases.

Most of the combustible gases and vapors listed in tables 1, 2, 3, and 4 form explosive mixtures when combined with air in certain definite proportions; however, there are a few combustible vapors, for example methylene chloride and trichloroethylene, that are incapable of producing explosive mixtures with air because the oxygen content is too low. In pure oxygen they have very wide explosive limits and generate considerable pressure on explosion in closed containers.

The fact that all combustible gases and vapors will not burn or explode when the oxygen content is reduced below certain definite values that vary with the combustible under consideration offers a means of controlling and eliminating explosion hazards in closed spaces. Below are given the oxygen values below which explosions cannot take place for several typical combustible gases and vapors:

	Oxygen, percent		Oxygen, percent
Natural gas ..	12.0	Pentane	12.1
Methane	12.1	Hexane	11.9
Ethane	11.0	Ethylene	10.0
Propane.....	11.4	Propylene	11.9
Butane	12.1	Carbon monoxide....	5.6
		Hydrogen	5.0

It appears impossible to take advantage of oxygen control in the prevention of explosions in rescue work because of the fact that most operations will take place where normal air is present.

Sources of Ignition

A third factor is ignition sources. Combustible gases and vapors may be present as well as air in the right proportions to give explosive mixtures and yet be free of explosion hazards, provided all sources of ignition are eliminated. Ignition sources may be classified as (1) flames, (2) sparks, and (3) heated materials.

In large surface disasters, ignition sources are usually present in the form of electric short circuits, arcs, fires, etc.; in bombing raids,

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certainly always in the form of incendiary bombs. The rescue worker may assume, therefore, that combustible gases of various types will be present after any extensive air raid, and may be present after any extensive surface disaster, that the necessary oxygen will be supplied by the atmosphere, and that ignition sources are likely to be present.

The question then arises as to what rescue workers may do to mitigate the explosion hazards that may be present. A partial answer to this is given under the discussion of a fourth factor, which deals with the distribution of oxygen and combustibles.

Distribution of Oxygen with Respect to the Combustibles

This is perhaps the most important factor in the prevention of explosions after disasters.

As an example of how this factor operates, let us consider the operation of an ordinary gas-range burner, with which everyone is familiar. When we turn on and light the gas with a match, we are not unduly alarmed because we know that, when ignited on contact with air, undiluted gas merely burns as it emerges from the burner ports. No explosion results from this operation for the reason that we are keeping the gas on one side of the fence and the oxygen supply on the other. The mixture does not explode because the gas has not had the time or the opportunity to mix thoroughly with the air surrounding the flame. Likewise, liquid gasoline in an open container is not especially dangerous. If the vapor above the liquid is ignited, it merely burns with a yellow sooty flame and without explosive violence, however, if we take a proper portion of the liquid and shake it up with air in a closed container so that the gasoline vapor becomes thoroughly diffused and in intimate contact with the air an exceedingly violent explosion results when the mixture is ignited.

It is therefore the primary duty of rescue workers, insofar as they are able to prevent the accumulation of explosive mixtures of combustible gases and vapors with air.

Ways to Prevent Mixing of Cumbustibles and Oxygen

1. If gas is burning at leaks or liquid combustibles are burning on the ground, where such fires can do no particular damage, do not extinguish the flame. Let the combustibles continue to burn. Burning consumes the gas and prevents the possible creation of explosive atmospheres in the surrounding area.

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2. The vapors given off by all combustible liquids are heavier than air. Gasoline vapor, for example, is about 3.5 times as heavy. The concentrated vapor will flow more or less like water along the floor and ground and settle in low places. Remove the liquid and vapors, if possible, with a minimum amount of disturbance. To attack with streams of water spreads the hazard and creates widespread explosive mixtures. The immediate necessity is to prevent the liquid combustibles from spreading to other areas. Dirt, ashes, lime, cement, or sawdust may be put on the pools of liquid to absorb it and keep it from spreading and vaporizing.

If combustible liquid accumulates in cellars, tunnels, or manholes there is no easy way of getting rid of it. Buckets may be used to bail it out, followed by mops to absorb the remaining liquid. No attempt should be made to ventilate spaces containing combustible liquids until after all liquid residues have been removed.

GENERAL COMMENTS

Danger of explosions occurring from gas leaks in the open air is remote. Almost all fuel gases are lighter than air and tend to rise at the point of leakage. Because of the unlimited supply of air surrounding the leaking gas, the mixtures are diluted rather quickly to the point where they are below the lower explosive limit, except at the point of discharge.

In closed spaces with little ventilation, rapid diffusion of leaking gas into the space may create an explosive condition within a very short time. Rescue workers should be exceedingly cautious when entering closed rooms, buildings, cellars, manholes, tunnels, and other underground areas; no one should enter until the atmosphere has been tested and found to be free of explosion hazards.

Testing for an explosive condition may be accomplished in various ways, depending upon the means available. Combustible gas indicators often form a part of the regular equipment of public utility, mining, and manufacturing companies. These instruments are designed to indicate directly whether an atmosphere is flammable or not.

Explosion and toxic hazards are largely eliminated when one wall of a building or the doors and windows have been blown out. The increased ventilation will keep the spaces below the lower explosive limit except near very large gas leaks.

When entering and working in a closed space, open or remove, if necessary, all doors and windows.

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Upon explosion, gaseous mixtures expand to 4 to 6 times their original volume, and workers at considerable distances from the seat of the explosion may be burned or injured.

All open lights, smoking, and nonpermissible[3/] electrical equipment should be barred from areas where combustible and explosive mixtures may be present.

3/ Nonpermissible electrical equipment is that which has not been investigated and approved by the Bureau of Mines for use in gassy atmospheres.

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